

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
31 January 2002 (31.01.2002)

PCT

(10) International Publication Number
WO 02/09103 A1

(51) International Patent Classification⁷: G11B 7/26 (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(21) International Application Number: PCT/NL01/00472

(22) International Filing Date: 25 June 2001 (25.06.2001)

(25) Filing Language: Dutch

(26) Publication Language: English

(30) Priority Data: 1015524 26 June 2000 (26.06.2000) NL

(71) Applicant (for all designated States except US): OTB GROUP B.V. [NL/NL]; Dillenburgstraat 29, NL-5652 AM Eindhoven (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): HENDRIKS, Christian, Etienne [NL/NL]; Busweg 28, NL-5632 PM Eindhoven (NL). TACKEN, Roland, Anthony [NL/NL]; Jan Tooropstraat 22, NL-5642 AK Eindhoven (NL).

(74) Agents: PRINS, A., W. et al.; c/o VEREENIGDE, Nieuwe Parklaan 97, NL-2587 BN The Hague, NL-5612 LV Eindhoven (NL).

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

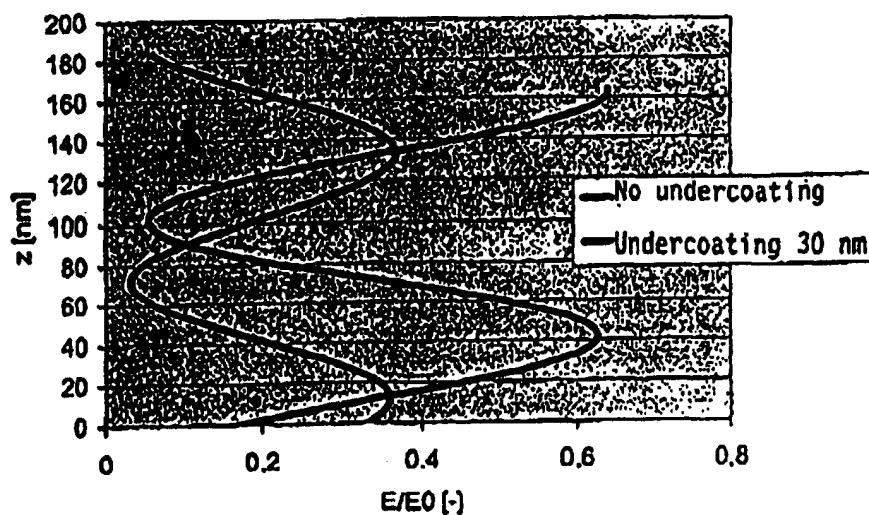
— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A METHOD FOR MANUFACTURING A SUBSTRATE FOR USE IN A STAMPER MANUFACTURING PROCESS, AS WELL AS A SUBSTRATE OBTAINED BY USING SUCH A METHOD



WO 02/09103 A1



(57) Abstract: The present invention relates to a method for manufacturing a substrate for use in a stamper manufacturing process. The present invention furthermore relates to a substrate which is used in a stamper manufacturing process and to a method for manufacturing a stamper to be used in producing optical discs, comprising the exposing, developing and heating of a photosensitive film that has been coated onto a substrate.

A method for manufacturing a substrate for use in a stamper manufacturing process, as well as a substrate obtained by using such a method.

5 The present invention relates to a method for manufacturing a substrate for use in a stamper manufacturing process. The present invention furthermore relates to a substrate which is used in a stamper manufacturing process and to a method for manufacturing a stamper to be used in producing optical discs, comprising the exposing, developing and
10 heating of a photosensitive film that has been coated onto a substrate.

From JP-58-077044 there is known a method for enhancing the contact intensity of a photoresist film by producing a crosslinking reaction after applying a thin photoresist coating to a glass substrate or to a reflective film present on the substrate. Thus a reflective film
15 is first formed on a glass substrate, after which a photoresist film is coated thereon in a thickness of about 100 Å. By increasing the temperature, a cross-linking reaction is produced between said two films, and a photoresist film having a thickness of about 1,000 Å is coated onto the thus cross-linked films, followed by exposure and development
20 thereof. The said publication does not provide any information as regards the influence of the crosslinked undercoating on the photoresist film that is finally to be exposed and developed.

Optical discs contain information that is recorded in a geometric structure. More in particular, said geometric structure
25 consists of pits and lands, which pits are arranged in concentrical circles or in a spiral in a surface of a respective optical disc. Also grooves are used as the structure of optical discs. When large numbers of such optical discs are to be produced, however, a stamper is placed in the mould of an injection moulding machine, after which the optical discs
30 are finally metallized and provided with a protective lacquer and a label or print.

The stamper manufacturing process as referred to in the introduction is known per se from the prior Dutch patent applications nos. 9400225 and 1007216 filed in the name of the present applicant, according to which process an unstructured stamper plate is prepared, 5 which preparation comprises the cleaning and possible coating of an adhesion layer for the photoresist that is yet to be coated. Subsequently, a negative photoresist is coated onto a thus prepared, unstructured stamper plate, which photoresist is selectively exposed to laser light, after which the selectively exposed photoresist film is 10 heated and subsequently integrally exposed. Finally, the integrally exposed photoresist is developed so as to provide the structured photoresist film, which is subsequently heated. In the direct stamper recording (DSR) process that is currently used, in respect of which the present applicant was granted Dutch patent no. 1009106 before, a stamper 15 is formed directly on a nickel substrate by means of a galvanic process. The substrate that is used thereby actually consists of a circular nickel disc having a diameter of about 200 μm and a thickness of about 300 μm , onto which disc a novolak-based photoresist has been coated, using an adhesion layer. The function of said adhesion layer, which, on account of 20 its thickness, can only be considered to be a "monolayer", is to form a suitable surface onto which the novolak-based photoresist can be coated. In the subsequent step of the DSR process, the photoresist film that has been coated onto the substrate is selectively exposed by means of laser light, and subsequently heated and integrally exposed. Following the developing step, removal of the photoresist takes place, with the exception of the photoresist posts that remain behind on the nickel substrate. Said photoresist posts are subsequently hardened by using an exposure step with a wavelength in the deep UV region, followed by a heating step at a high temperature (hard bake) so as to strengthen the exposed, and thus crosslinked, regions additional by further crosslinking 25 of polymer chains. A stamper obtained by using such a method thus 30

comprises a nickel shell including photoresist posts. Further hardening of the photoresist posts makes it possible to produce at least 5000 replicas by means of such a stamper, which is used in the mould of an injection moulding machine for mass-producing CD replicas.

5 Research has shown that defects, such as stripes and stains, may be introduced on the surface of the nickel substrate during the galvanic process. In some cases said defects can be detected on an unprocessed nickel substrate by means of halogen light. After the above-described processing steps in the DSR process, however, such defects will
10 show up. This phenomenon is assumed to be caused by a local difference in the diffraction pattern, which pattern is formed by the structure of photoresist posts. Not only the human eye is very sensitive to differences in the diffraction pattern, but also the electric signal from the stamper can be influenced by the quality of the substrates.

15 Additional research has moreover shown that standing waves occur in the photoresist film during the exposure step of the stamper manufacturing process. Said standing waves, which are caused by reflection of the substrate, result in the occurrence of alternating high and low exposure energy levels in the thickness of the resist, as a
20 result of which photoresist posts of irregular shape and dimensions are eventually obtained, which is undesirable.

25 The object of the present invention is thus to manufacture a substrate for use in a stamper manufacturing process, in particular in the DSR process, wherein the quality of the substrate in the stamper that is eventually produced is of secondary importance.

 Another object of the present invention is to provide a stamper, which stamper has an extended technical life span in comparison with the DSR stampers that are currently commercially available.

30 Another object of the present invention is to provide a method for manufacturing a substrate for use in a stamper manufacturing process, wherein it is possible to abandon the monolayer that is

currently being used as an adhesive.

Yet another object of the invention is to provide a method for manufacturing a substrate for use in a stamper manufacturing process, which method is carried out in such a manner that the negative effect of standing waves, in particular the position of the interference curve, on the formation of the photoresist posts is minimized.

The method as referred to in the introduction is according to the present invention characterized in that the method comprises the following steps:

10 a) coating a crosslinkable chemical composition onto the substrate;

b) subjecting the undercoating applied in step a) to a crosslinking reaction; and

15 c) applying a top coating of a photosensitive material to the undercoating that has been crosslinked in step b), wherein the thickness of the crosslinked undercoating of step b) is selected so that the maximum energy intensity during the exposure step of the stamper manufacturing process occurs at the desired post height of the top coating that is to be developed.

20 As already said before, the light that falls onto the substrate undergoes an endless number of reflections at the interface between the resist and the surrounding atmosphere, and also at the interface between the resist and the substrate. Said entering and exiting light waves interfere in the resist, and a so-called interference curve is formed, which interference leads to a variation in the intensity of the energy that the resist receives across the thickness of the film layer. By selecting the thickness of said undercoating, in accordance with the present invention, so that the maximum energy intensity during the exposure step of the stamper manufacturing process occurs at the desired post height of the photoresist posts of the top coating that is to be developed, the position of the interference curve is shifted so

that the maximum value of the destructive interference does not occur in the region of the desired post height. Thus a top coating is obtained from which reproducible photoresist posts having a desired height and a desired shape can be obtained.

5 A novolak-based photoresist is preferred as said suitable, crosslinkable chemical composition. In addition to that it is also possible in specific embodiments to use a material which comprises novolak, for example pure novolak.

10 It is in particular preferred to carry out step b) by using a heat treatment, in particular at a temperature ranging from 150 - 250 °C. Such a temperature range will result in three-dimensional crosslinking of the polymer chains of the chemical composition provided in step a), which undercoating will mask any defects in the substrate.

15 According to a special embodiment of the present method, step b) is carried out by using an exposure step, in particular in the wavelength range of 200 - 320 nm.

20 The exposure time is in particular 5 - 180 seconds, whereby the exposure step is carried out in particular while rotating and/or heating the substrate. Since the crosslinkable chemical composition has undergone a crosslinking reaction in step b), the thus crosslinked composition is not soluble, or only to a small degree, in the solvent that is used in the photosensitive material that has been provided in step c).

25 According to the present method, the top coating is subjected to a heat treatment in an additional step d), which step d) is carried out at such a temperature that no crosslinking of the photosensitive material that has already been applied in step c) will take place. This means that step d) is in particular carried out at a temperature of maximally 130 °C. The solvent that is present in the top coating is removed by carrying out step d).

30 For the present invention it is in particular important

that no crosslinking reaction will take place in the top coating of the photosensitive material, because said top coating will be structured in the further DSR process so as to form the above-described photoresist posts.

5 In a special embodiment it is desirable to subject the substrate to a preparation step prior to carrying out step a), which preparation step comprises the cleaning of the substrate and possibly the application of an adhesion layer for the crosslinkable chemical composition that is to be applied in step a).

10 The object of such a preparation step is in particular to improve the adhesion between the substrate and the undercoating that is to be provided in step a), whereby the undercoating is thus present on the adhesion layer that has been applied to the substrate previously.

15 Preferably, a metal is used for the substrate, in particular nickel.

20 In order to obtain layers having a uniform thickness, it is preferred to carry out step a) as well as step c) by means of a spin-coating process, whereby the crosslinkable chemical composition that is coated onto the substrate in step a) may be the same as the photosensitive material that is applied in step c).

25 The present invention furthermore relates to a substrate for use in a stamper manufacturing process, which substrate is according to the present invention characterized in that it successively comprises an undercoating of a crosslinked chemical composition and a top coating of a photosensitive material, wherein in particular the thickness of said undercoating is in the order of 10 - 100 nm and wherein the thickness of the top coating is in the order of 150 - 250 nm, preferably 150 - 200 nm. The height of the photoresist posts is preferably 100 - 150 nm, in particular 120 - 130 nm.

30 The present substrate is in particular suitable for use in a method for manufacturing a stamper, which stamper is placed in the

mould of an injection moulding machine for mass-producing CD replicas, and such a method comprises the exposing, developing and heating of the photosensitive layer which has been coated onto the substrate in step c).

5 The present invention will be explained in more detail hereafter with reference to a number of figures, which figures should not be taken to be limitative, they merely function to illustrate the present invention.

Figure 1 shows the shape of a photoresist post as obtained by using a substrate not provided with an undercoating.

10 Figure 2 shows the shape of another photoresist post as obtained by using a substrate not provided with an undercoating.

Figure 3 shows the shape of a photoresist post as obtained by using a substrate provided with an undercoating.

15 Figure 4 shows the interference curve of two embodiments, in particular of a substrate comprising an undercoating and of a substrate which does not comprise an undercoating.

20 Figure 1 shows an example of a photoresist post wherein the standing wave effect as measured by means of AFM is clearly visible. The nickel substrate was provided with a photoresist having a thickness of 165 nm, the height of the photoresist posts obtained after exposure and development is 129 nm. Due to the absence of an undercoating, a photoresist post of highly irregular shape has been obtained, which is undesirable in practice.

25 Figure 2 schematically shows a photoresist post wherein the standing wave effect as measured by means of AFM is clearly visible. Present on the nickle substrate was a photoresist film having a thickness of 165 nm, with the height of the photoresist post being 121 nm. Figure 2 clearly shows that a photoresist post of erratic dimensions is obtained if no undercoating is used.

30 Figure 3 schematically shows a photoresist post wherein a nickel substrate having an undercoating of 30 nm and a resist layer of

185 nm was used. The height of the photoresist post was 122 nm. From this schematic illustration it is apparent that the use of an undercoating of the desired thickness has resulted in a shift of the position of the interference curve, which new position has led to a reproducible, smooth photoresist post.

5 Figure 4 shows the shift of the interference curve resulting from the use of an undercoating on a substrate. Set off on the vertical axis is parameter z , which parameter indicates the distance perpendicularly to the substrate, wherein the value $z = 0$ corresponds to 10 the substrate area. Set off on the horizontal axis is the energy intensity, wherein E_0 is the intensity at the resist surface, which has value 1. From Figure 4 it follows that the use of an undercoating having 15 a thickness of 30 nm has resulted in a shift of the position of the interference curve, wherein the maximum energy intensity occurs in particular in the region of the desired height of the photoresist post, viz. 120 - 130 nm.

CLAIMS

1. A method for manufacturing a substrate for use in a stamper manufacturing process, characterized in that said method comprises the following steps:

5 a) coating a crosslinkable chemical composition onto the substrate;

b) subjecting the undercoating applied in step a) to a crosslinking reaction; and

10 c) applying a top coating of a photosensitive material to the undercoating that has been crosslinked in step b), wherein the thickness of the crosslinked undercoating of step b) is selected so that the maximum energy intensity during the exposure step of the stamper manufacturing process occurs at the desired post height of the top 15 coating that is to be developed.

2. A method according to claim 1, characterized in that a novolak-based photoresist is used as said suitable, crosslinkable chemical composition.

3. A method according to claims 1 - 2, characterized in that 20 said method furthermore comprises an additional step d), viz.:

d) subjecting the top coating applied in step c) to a heat treatment.

4. A method according to claims 1 - 3, characterized in that step b) is carried out by using a heat treatment, in particular at a 25 temperature ranging from 150 - 250 °C.

5. A method according to claims 1 - 3, characterized in that step b) is carried out by using an exposure step.

6. A method according to claim 5, characterized in that said exposure step is carried out in the wavelength range of 200 - 320 nm.

30 7. A method according to claims 5 - 6, characterized in that the exposure time is 5 - 180 seconds.

8. A method according to claims 5 - 7, characterized in that said exposure step is carried out while rotating the substrate.

9. A method according to claims 5 - 8, characterized in that said exposure step is carried out while heating the substrate.

5 10. A method according to claims 1 - 9, characterized in that a layer thickness in the order of 10 - 100 nm is used for said undercoating in step a).

10 11. A method according to claims 1 - 10, characterized in that a layer thickness in the order of 150 - 250 nm, in particular 150 - 200 nm, is used for the top coating in step c).

12. A method according to claims 3 - 11, characterized in that step d) is carried out at such a temperature that no crosslinking of the photosensitive material that has been applied in step c) takes place.

13. A method according to claim 12, characterized in that step 15 d) is carried out at a temperature of maximally 130 °C.

14. A method according to claims 1 - 13, characterized in that the substrate is subjected to a preparation step prior to carrying out step a), which preparation step comprises the cleaning of the substrate and possibly the application of an adhesion layer for the crosslinkable chemical composition that is to be applied in step a).

15. A method according to claims 1 - 14, characterized in that a metal is used for the substrate, in particular nickel.

16. A method according to claims 1 - 15, characterized in that the crosslinkable chemical composition that is coated onto the substrate 25 in step a) may be the same as the photosensitive material that is applied in step c).

17. A method according to claims 1 - 16, characterized in that step a) as well as step c) are carried out by means of a spin-coating process.

30 18. A substrate for use in a stamper manufacturing process, characterized in that said substrate successively comprises an

undercoating of a crosslinked chemical composition and a top coating of a photosensitive material.

19. A substrate according to claim 18, characterized in that a novolak-based photoresist is used as said crosslinkable chemical composition.

20. A substrate according to claims 18 - 19, characterized in that said substrate is a metal, in particular nickel.

21. A substrate according to claims 18 - 20, characterized in that the thickness of said undercoating is 10 - 100 nm.

10 22. A substrate according to claims 18 - 21, characterized in that the thickness of said top coating is 150 - 250 nm, in particular 150 - 200 nm.

15 23. A method for manufacturing a stamper for producing optical discs, comprising the exposing, developing and heating of a photosensitive layer which has been coated onto a substrate, characterized in that the substrate according to the method defined in claims 1 - 17 or the substrate according to claims 18 - 22 is used.

1/1

Figure 1

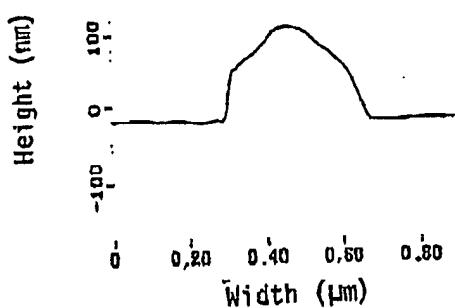


Figure 2

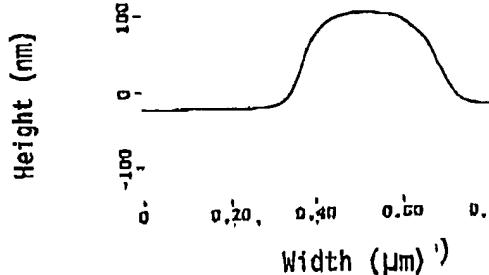
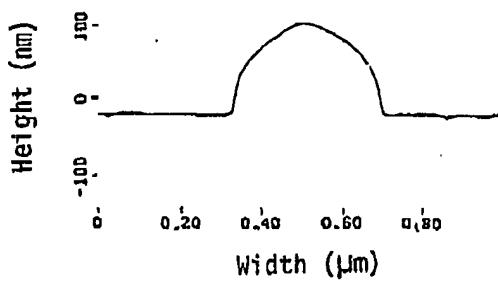


Figure 3

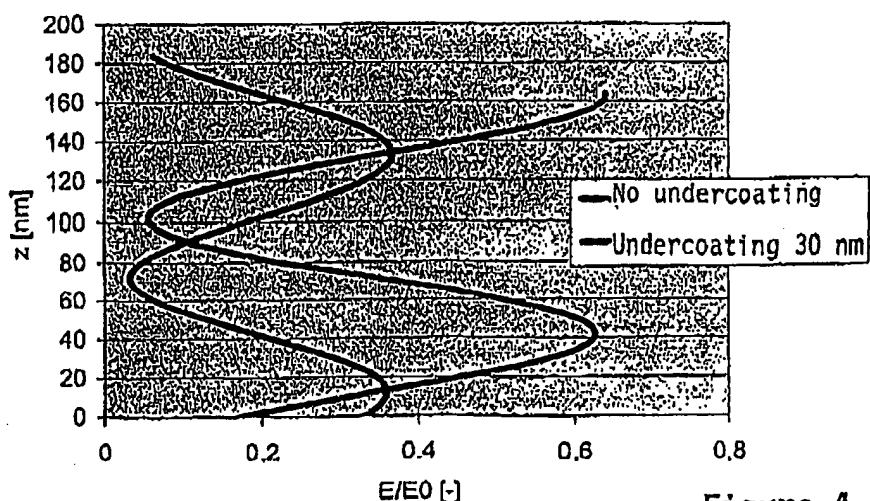


Figure 4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 01/00472A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G11B7/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 007, no. 172 (P-213), 29 July 1983 (1983-07-29) -& JP 58 077044 A (SANYO DENKI KK), 10 May 1983 (1983-05-10) abstract	1,4, 10-13, 18,23
Y		14,15, 17,20
A		2,3,5, 21,22
Y	EP 0 667 608 A (OD & ME BV) 16 August 1995 (1995-08-16) cited in the application abstract page 4, line 34 - line 35 page 5, line 29 - line 35	14,17
		-/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

- *T* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search 21 September 2001	Date of mailing of the International search report 28/09/2001
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patenttaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Authorized officer Annibal, P

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 01/00472

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 97 37348 A (BIFANO THOMAS G) 9 October 1997 (1997-10-09) abstract	15,20
A	WO 99 18572 A (OD & ME BV ;ENGELEN THOMAS WILHELMUS (NL); STALS WALTER THEODORUS) 15 April 1999 (1999-04-15) cited in the application the whole document	1-23
A	EP 0 596 439 A (MATSUSHITA ELECTRIC IND CO LTD) 11 May 1994 (1994-05-11) the whole document	1-23
A	WO 99 52105 A (IMATION CORP) 14 October 1999 (1999-10-14) abstract page 13, line 13 - line 20	1,14
A	EP 0 660 314 A (PHILIPS ELECTRONICS NV) 28 June 1995 (1995-06-28) abstract column 12, line 16 - line 25	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No
PCT/NL 01/00472

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
JP 58077044	A	10-05-1983	NONE		
EP 0667608	A	16-08-1995	NL AT CN DE DE EP ES HK JP SG US	9400225 A 187010 T 1121240 A , B 69513424 D1 69513424 T2 0667608 A1 2140613 T3 1003736 A1 7326077 A 52782 A1 6159664 A	01-09-1995 15-12-1999 24-04-1996 30-12-1999 23-03-2000 16-08-1995 01-03-2000 30-06-2000 12-12-1995 28-09-1998 12-12-2000
WO 9737348	A	09-10-1997	US AU BR CA CN EP JP WO	5783371 A 2603097 A 9710414 A 2250543 A1 1220759 A 0891621 A1 2000507734 T 9737348 A1	21-07-1998 22-10-1997 11-01-2000 09-10-1997 23-06-1999 20-01-1999 20-06-2000 09-10-1997
WO 9918572	A	15-04-1999	NL AU EP WO	1007216 C2 9560698 A 1027702 A1 9918572 A1	08-04-1999 27-04-1999 16-08-2000 15-04-1999
EP 0596439	A	11-05-1994	JP JP EP	6150391 A 6150397 A 0596439 A2	31-05-1994 31-05-1994 11-05-1994
WO 9952105	A	14-10-1999	CN DE GB WO US US	1295711 T 19983100 T0 2350205 A 9952105 A1 2001000746 A1 2001016301 A1	16-05-2001 31-05-2001 22-11-2000 14-10-1999 03-05-2001 23-08-2001
EP 0660314	A	28-06-1995	BE EP AT CN DE DE JP US US	1007912 A4 0660314 A1 198386 T 1119323 A 69426482 D1 69426482 T2 7320308 A 5605782 A 5790512 A	14-11-1995 28-06-1995 15-01-2001 27-03-1996 01-02-2001 12-07-2001 08-12-1995 25-02-1997 04-08-1998